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Determination of urban volatile organic compound emission ratios and comparison with an emissions database

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[1] During the NEAQS-ITCT2k4 campaign in New England, anthropogenic VOCs and CO were measured downwind from New York City and Boston. The emission ratios of VOCs relative to CO and acetylene were calculated using a method in which the ratio of a VOC with acetylene is plotted versus the photochemical age. The intercept at the photochemical age of zero gives the emission ratio. The so determined emission ratios were compared to other measurement sets, including data from the same location in 2002, canister samples collected inside New York City and Boston, aircraft measurements from Los Angeles in 2002, and the average urban composition of 39 U.S. cities. All the measurements generally agree within a factor of two. The measured emission ratios also agree for most compounds within a factor of two with vehicle exhaust data indicating that a major source of VOCs in urban areas is automobiles. A comparison with an anthropogenic emission database shows less agreement. Especially large discrepancies were found for the C₂-C₄ alkanes and most oxygenated species. As an example, the database overestimated toluene by almost a factor of three, which caused an air quality forecast model (WRF-CHEM) using this database to overpredict the toluene mixing ratio by a factor of 2.5 as well. On the other hand, the overall reactivity of the measured species and the reactivity of the same compounds in the emission database were found to agree within 30%.

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1. Introduction

[2] Volatile organic compounds (VOCs) are emitted into the atmosphere in large quantities from a variety of different natural and anthropogenic sources [Brasseur *et al.*, 1999; Hewitt, 1999]. VOCs are key ingredients in the formation of ozone and aerosols in polluted air, and play a significant role in determining regional air quality, in the chemistry of the global troposphere, and possibly in the global carbon cycle. On a global scale the biogenic VOC emissions, mainly isoprene, α - and β -pinene and methanol [Guenther *et al.*, 1995, 2006], dominate over the anthropogenic sources. On a regional scale, in and around urban areas, the anthropogenic emissions, which are in large part caused

by-production, storage and use of fossil fuels, usually are more important.

[3] In July and August of 2004, a large-scale atmospheric chemistry and transport study was conducted over North America and Europe within the framework of the ICARTT collaboration (International Consortium for Atmospheric Research on Transport and Transformation). As part of the NOAA contribution to ICARTT, the NEAQS-ITCT 2k4 (New England Air Quality Study–Intercontinental Transport and Chemical Transformation) study was conducted, which involved airborne measurements using the NOAA WP-3 research aircraft based out of Portsmouth, New Hampshire and ship-based measurements using the NOAA research vessel *Ronald H. Brown* in the Gulf of Maine. Research goals of the NEAQS-ITCT 2k4 study included a detailed characterization of (1) the primary emissions of gas phase and aerosol species on the North American continent, including emissions from eastern U.S. cities (Boston and New York City), forest vegetation, and point sources such as power plants; (2) the chemical transformation leading to the formation of secondary pollutants (ozone and aerosol); (3) the transport processes involved, including local and long-range transport to Europe; and (4) the evaluation of air quality forecast models.

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[4] The quality of the forecast of ozone and secondary organic aerosol (SOA) formation strongly depends on the accurate knowledge of the primary VOCs emissions that act as precursors for ozone and SOA. Extensive data sets that provide gridded VOC emissions of a large number of species are used in these models. Recent examples for the importance of the accurate knowledge of anthropogenic emission data sets for air quality forecasts are modeling papers for the Houston area [Jiang and Fast, 2004; Lei *et al.*, 2004; Zhang *et al.*, 2004].

[5] In this paper, we will focus on the determination of primary anthropogenic VOC emission ratios from mainly Boston and New York City. Emission ratios of a large number of VOCs versus acetylene and CO will be determined using the ship-based measurements in the Gulf of Maine downwind of the urban areas. The resulting emission ratio data will be compared to data from a previous campaign in 2002 in the same area, to canister samples collected in Boston and New York City and to data from Los Angeles in 2002. The measured emission ratios will also be used to test an anthropogenic emissions database, which is based on the EPA NEI-99 (Environmental Protection Agency National Emissions Inventory-99) database. This database includes four categories of emissions: on-road, off-road, area and point sources. We will compare our results to the sum of those four categories, because the VOC measurements were made downwind of the urban areas and should include all the source categories. The database is used in various regional air quality forecast models such as the WRF-CHEM (Weather Research and Forecasting-Chemical Model). The results from WRF-CHEM are compared to the measurements from the NEAQS-ITCT 2k4 study to demonstrate that the use of too high emission ratios will cause an overprediction in the model result.

2. Methods

2.1. Measurements

[6] The NOAA research vessel *Ronald H. Brown* (RHB) operated in the Gulf of Maine between Boston, Massachusetts, and Nova Scotia from 5 July until 12 August 2004. The NOAA WP-3 aircraft conducted 18 research flights between 5 July and 15 August 2004, from Portsmouth, New Hampshire. The RHB and the WP-3 both carried an extensive set of instruments to characterize the gas phase and aerosol properties of the atmosphere. A full description of the payload of the WP-3 and the RHB will be given elsewhere. Here only the relevant instruments are described briefly.

[7] The measurements from Los Angeles were performed using the WP-3 aircraft as part of the ITCT2k2 (Intercontinental Transport and Chemical Transformation 2002) study [Nowak *et al.*, 2004]. The same relevant instrumentation as described below was used on the WP-3 during this campaign.

2.1.1. Ship-Based Instrumentation

[8] VOC measurements on the RHB were performed using an online GC-MS. A detailed description of this instrument and its analysis procedure is given elsewhere [Goldan *et al.*, 2004]. The GC-MS instrument analyzed 350 mL air samples with a 5-min acquisition time every 30 min. More than 100 VOCs including many oxygenated

compounds, hydrocarbons, halocarbons and alkyl nitrates were identified and quantified with this instrument. The detection limit of the GC-MS instrument is <0.5 pptv and the measurement precision is about 2%. The overall accuracy is mainly dependent on the quality of the calibration standards used and is within 10% [Goldan *et al.*, 2004].

[9] CO was measured via a modified AeroLaser GmbH [Garmisch-Partenkirchen, Germany] AL5002 Ultra-Fast CO analyzer, a commercially available vacuum-UV resonance fluorescence instrument [Gerbig *et al.*, 1999]. For the campaign, data were collected at 1 Hz and averaged to a 1-min resolution; the total uncertainty is estimated at 3%, with a limit of detection of 1.5 ppbv.

2.1.2. Airborne Instrumentation

[10] High time resolution measurements of oxygenated VOCs, aromatics, acetonitrile, isoprene and monoterpenes were made on the WP-3 aircraft with a PTR-MS instrument from Ionicon Analytik [de Gouw *et al.*, 2003a]. VOCs were measured for 1 s every 17 s. During a ship-based intercomparison PTR-MS measurements have been compared with the online GC-MS instrument [de Gouw *et al.*, 2003b], and possible interferences have been studied by combining PTR-MS with a gas chromatographic pre separation method [de Gouw *et al.*, 2003a, 2003c; Warneke *et al.*, 2003]. For a detailed description of the PTR-MS instrument, the reader is referred to these references. The PTR-MS was calibrated for many VOCs between the flights using a standard mixture containing 500 ppbv of each compound that was diluted to sub-ppbv levels. The calibration accuracy is estimated to be better than 15% for each compound. The detection limit of the PTR-MS is dependent on the compound and ranges from 30 pptv to 340 pptv [de Gouw *et al.*, 2006].

[11] During every flight, up to 80 whole air samples (WAS) were collected in electropolished stainless steel gas canisters. The canisters were filled within 5 s to 15 s dependent on the altitude at variable intervals. The canisters were transported to the NCAR laboratory in Boulder, where they were analyzed within a few days for hydrocarbons, halocarbons and C_1 - to C_5 - alkyl nitrates using several gas chromatography techniques. The sampling and the subsequent analysis of the canisters is described elsewhere [Schauffler *et al.*, 1999, 2003]. The overall accuracy for the VOC measurements is about 10% and the detection limit is about 5 pptv. In the analysis presented here mainly the acetylene measurements were used.

[12] CO was determined on the WP-3 aircraft every second using a vacuum ultraviolet fluorescence measurement [Holloway *et al.*, 2000]. The precision of the measurements is estimated to be 2.5%. Variability in the determination of zero levels results in an absolute uncertainty of about 1 ppbv in the values reported. The field standard was compared to NIST Standard Reference Material (SRM) 2612a (10 ppmv nominal CO in air). The concentration of the calibration standard is known to within 2%. The overall accuracy of the 1 s measurements is thus estimated to be 5%.

2.2. Anthropogenic Emissions Database

[13] The anthropogenic VOC emissions database (4 km horizontal resolution) is based upon the U.S. EPA's 1999 National Emissions Inventory (NEI-99, version 3) released November 2003 (updated to March 2004 revisions), and the

4 km horizontal resolution spatial surrogates released by EPA in September of 2003. The emissions are representative of a typical summer day (average of weekday and weekend days). VOC and PM_{2.5} compounds, along with the 7 primary species are divided into 24 average hourly emissions. This database is designed for regional-scale photochemical models of North America that require emissions data for NO_x, VOC, CO, SO₂, NH₃, PM_{2.5} and PM₁₀. Spatial partitioning within the U.S. and Canadian provinces is based on spatial surrogates and source classification code (SCC) assignments recommended by the U.S. EPA. Anthropogenic VOCs are partitioned into 41 individual and lumped VOC compounds, with several of the lumped VOC compounds defined by the SAPRC-99 (Statewide Air Pollution Research Center) condensed photochemical mechanism [Carter, 2000]. A more detailed description of the anthropogenic emissions database is given by Frost *et al.* [2006] and the Web site within that reference (<http://ruc.fsl.noaa.gov/wrf/WG11/anthropogenic.htm>). The emission of a particular VOC from a single source involves a three-step process: each SCC specific VOC emission is converted to a total organic gas (TOG) emission, each SCC emission is linked to one of about 700 TOG profiles, and then each TOG profile is linked to about 760 individual VOC. The data sets used in each of these steps is available either directly through the U.S. EPA speciation Web site (<http://www.epa.gov/ttn/chief/emch/speciation/>) or through the SPECIATE version 3.2 software also available at that Web site. Emissions of several individual VOC (e.g., ethane, propane, ethylene, propylene, acetylene, styrene, benzene, toluene, acetone, and acetaldehyde) are extracted for the database, and are used for comparisons in this study. Emissions of the lumped VOC species are determined by aggregating the individual VOC following the condensed SAPRC-99 mechanism species assignments [Carter, 2000], excluding the individual VOC separated out before hand from their lumped categories.

2.3. NOAA WRF-CHEM Model

[14] The multiscale air pollution prediction system used here is based on the Weather Research and Forecasting (WRF) model, which is coupled with the RADM2 chemical mechanism [Stockwell *et al.*, 1990] with updated reaction rates and NO₃ chemistry consistent with the RACM mechanism [Stockwell *et al.*, 1997]. Biogenic and anthropogenic emissions, dry deposition, convective and turbulent chemical transport, photolysis, and advective chemical transport are all treated simultaneously with the meteorology “online.” WRF-CHEM results presented here are from the “reference case” simulations documented by Frost *et al.* [2006]. The model domain covers the eastern U.S. and southeastern Canada, and the 15 July to 15 August 2004 time period during the ICARTT 2k4 field experiment with 27 km horizontal resolution. Details of the model setup, meteorological initial and boundary conditions, and physical options used within WRF-CHEM are given by Frost *et al.* [2006]. Anthropogenic VOC emissions are based on the database described in the previous section with emissions aggregation into RADM2 species assignments [Stockwell *et al.*, 1990]. Boundary conditions for chemical species, and details of the numerical treatment of various transport, physical, photochemical, radiative and aerosol processes

are documented by Grell *et al.* [2005]. Statistical evaluations of WRF-CHEM model performance for O₃ relative to several other models during the ICARTT 2k4 study period are given by McKeen *et al.* [2005].

3. Results and Discussion

3.1. Determination of Emission Ratios

[15] VOC emission ratios are determined from data collected on board the RHB in the Gulf of Maine downwind of Boston and New York City. For this analysis all data in the Gulf of Maine were used and not filtered to select periods, when the ship was directly downwind of Boston and/or New York City and our analysis includes the whole northeastern seaboard. The two cities were the overwhelming sources for the periods with high VOC enhancements and therefore we call the emission sources in the following analysis Boston and New York City. The emission ratios are determined using a method that was introduced by de Gouw *et al.* [2005]. In this method, which will be summarized in the following, the ratio of a VOC with acetylene is plotted versus the photochemical age as is shown in Figure 1a for ethyl benzene. The photochemical age was estimated using the measured ratio between toluene to benzene in the sampled air as described by Roberts *et al.* [1984]:

$$\Delta t = \frac{1}{[OH](k_{\text{toluene}} - k_{\text{benzene}})} \times \left[\ln \left(\frac{[\text{toluene}]}{[\text{benzene}]} \right) \Big|_{t=0} - \ln \left(\frac{[\text{toluene}]}{[\text{benzene}]} \right) \right], \quad (1)$$

where k_{toluene} and k_{benzene} are the rate coefficients for the reaction with OH ($k_{\text{toluene}} = 5.63 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_{\text{benzene}} = 1.22 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) [Atkinson *et al.*, 2005]. [OH] is the average concentration of the hydroxy radical. The emission ratio of benzene and toluene ($\frac{[\text{toluene}]}{[\text{benzene}]} \Big|_{t=0}$) was set to 4.25 and determined by looking at fresh plumes from Boston and New York City during several flights with the WP-3 aircraft. Plumes were assumed to be fresh, when the NO_x/NO_y ratio was larger than 80%. During eight different flights 18 fresh plumes were encountered, 11 of which were sampled during the night. The value of 4.25 for $\frac{[\text{toluene}]}{[\text{benzene}]} \Big|_{t=0}$ seems rather large, but in recent years benzene emissions have decreased [Fortin *et al.*, 2005; Harley *et al.*, 2006]. The measured ratio will also depend on the time of year and on the measurement region.

[16] The [ethyl benzene]/[acetylene] ratio decreases by an order of magnitude over the course of two days, because the OH rate coefficient of ethyl benzene ($k = 7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) is larger than that of acetylene ($k = 0.83 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) [Atkinson *et al.*, 2005]. The data in Figure 1 can be described with:

$$\frac{[\text{VOC}]}{[\text{C}_2\text{H}_2]} = ER_{\text{VOC}} \times \exp[-(k_{\text{VOC}} - k_{\text{C}_2\text{H}_2})[\text{OH}]\Delta t], \quad (2)$$

with [VOC] and [C₂H₂] being the volume mixing ratios of a primary anthropogenic VOC (ethyl benzene in Figure 1) and acetylene, ER_{VOC} the emission ratio of the VOC with acetylene, k_{VOC} and $k_{\text{C}_2\text{H}_2}$ the rate coefficients of those

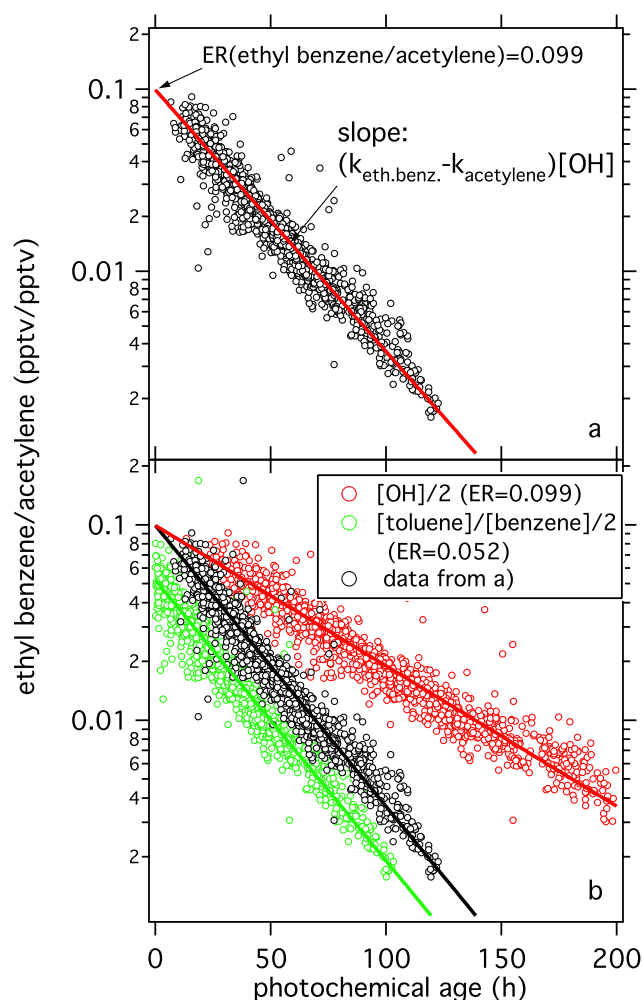


Figure 1. (a) Ethyl benzene/acetylene ratio plotted versus the photochemical age of the air mass. The measurements include all data on the RHB from 5 July until 12 August 2004 filtered for biomass burning and power plants ($N = 1608$). The red line is a linear fit where the emission ratio is determined at photochemical age zero. (b) Emission ratios determined using photochemical ages determined with $\text{OH}/2$ (red points with the red line as linear fit) and $\frac{[\text{toluene}]}{[\text{benzene}]}|_{t=0}/2$ (green points with the green line as linear fit). The black points and the black line are the data from Figure 1a.

compounds with OH [Atkinson *et al.*, 2005] and Δt the photochemical age. In Figure 1a $[\text{OH}]$ was set to $2.1 \times 10^6 \text{ molecules cm}^{-3}$, which was calculated for this data set in the same way as described by Warneke *et al.* [2004].

[17] From the intercept on the y axis of the linear fit (red line in Figure 1a) the emission ratio ER_{VOC} and from the slope k_{VOC} can be determined as described by equation (2). For this method of determining the emission ratios four assumptions must be valid:

[18] 1. The speciation of VOCs is the same for all sources upwind of the measurement area. For the presented data set the VOC sources are mainly Boston and New York City. The magnitude of the emission is proportional to the emission of acetylene, which is used here as an inert tracer. Acetylene is emitted mainly by automobile exhaust [Fortin

et al., 2005; Harley *et al.*, 1997]. Small other sources of acetylene, such as welding, certain chemical industries, and fires, might exist, but are assumed to be of little influence [Makar *et al.*, 2003; Whitby and Altwicker, 1978]. Regional differences in the VOC speciation are generally small as will be shown in this paper. The RHB is an ideal platform to study the emission ratios of Boston and New York City, because the urban plumes are usually transported mainly over the ocean before being encountered at the ship and therefore no fresh anthropogenic VOCs are added to the plumes during the transport. The air masses measured at the ship's location are frequently influenced by both Boston and New York City simultaneously and therefore the emissions from the two cities cannot be separated.

[19] 2. The removal of VOCs is controlled only by reactions with OH radicals. Reactions of VOCs with NO_3 radicals at night and with ozone were a minor sink of anthropogenic VOCs in the Gulf of Maine [Warneke *et al.*, 2004]. Some of the alkenes react with NO_3 , but their loss is small compared to the OH loss [Warneke *et al.*, 2004]. Losses due to wet and dry deposition are assumed to be negligible.

[20] 3. Anthropogenic/urban emissions are the only sources of the investigated primary hydrocarbons in this region. Other sources of VOCs and CO such as biomass burning and local sources (e.g., power plants and ship plumes) were observed but have been eliminated from this analysis. Biomass burning sources were eliminated by only considering data for which acetonitrile was lower than 150 pptv [Warneke *et al.*, 2006]. Power plant and ship plumes were eliminated by looking at CO and NO_x data combined with FLEXPART back trajectory calculations [Warneke *et al.*, 2006]. The total elimination excluded less than 10% of the data.

[21] 4. The photochemical age is described by formula (1). Limitations of using hydrocarbon ratios to determine the photochemical age by the mixing of air masses with a different age were pointed out in several studies [McKeen and Liu, 1993]. An error in the photochemical age results in a small error for the emission ratios as shown in Figure 1b. The black curve in Figure 1b is the same as in Figure 1a with the best estimate of the photochemical age. The red curve is with $[\text{OH}]$ reduced by a factor of 2 and the green curve has the $\frac{[\text{toluene}]}{[\text{benzene}]}|_{t=0}$ ratio set to 50% (2.125). Varying the $[\text{OH}]$ concentration has no effect on the resulting emission ratios. The initial estimate of the emission ratio of toluene versus benzene on the other hand, clearly has an influence. Toluene/benzene ratios depend on the fuel composition and must be carefully measured for this method and may be dependent on the location (different fuel types) and the time of year (different fuel composition in winter versus summer). We therefore estimate the error in the emission ratios to be about 30% (15% from the measurement uncertainty of benzene and toluene and additional 15% from the determination of the ratio).

[22] The emission ratios for all measured anthropogenic hydrocarbons versus acetylene determined in a manner similar to ethyl benzene as shown in Figure 1a are presented in Table 1 together with the emission ratios versus CO, which is used in many studies as the anthropogenic emissions marker instead of acetylene. Determining the emission

Table 1. Emission Ratios of Anthropogenic VOCs From Boston/New York City, Los Angeles, and an Anthropogenic Emissions Inventory Based on EPA Data^a

Compound	Boston/New York City 2004, pptv [pptv C ₂ H ₅] ⁻¹	Boston/New York City 2002, pptv [pptv C ₂ H ₅] ⁻¹	Boston/New York City CO 2004, pptv [ppbv CO] ⁻¹	Los Angeles 2002, pptv [ppbv CO] ⁻¹	Boston/New York City (Baker et al., submitted manuscript, 2006), pptv [ppbv CO] ⁻¹	39 US Cities [Seila et al., 1989], pptv [pptv C ₂ H ₅] ⁻¹	Vehicle Exhaust [Harley et al., 1992], pptv [pptv C ₂ H ₅] ⁻¹	Database, pptv [ppbv CO] ⁻¹
<i>Alkanes</i>								
Ethane	3.097	2.738	11.616	7.84	10.37	1.806	0.967	1.571
Propane	2.187	2.505	7.733	12.39	5.50	1.214	0.023	0.357
n-butane	0.482	0.660	1.688	5.4	2.39	1.562	0.758	
iso-butane	0.287	0.373	1.012	2.58	1.80	0.574	0.086	
n-pentane	0.463	0.555	1.548	3.01	1.69	0.682	0.250	
iso-pentane	1.192	1.509	3.991	6.38	3.65	1.404	0.583	
Cyclohexane	0.092	0.068	0.285			0.057	0	
Methyl cyclopentane	0.180	0.135	0.566			0.165	0.060	
n-hexane	0.335	0.175	1.072		1.13	0.284	0.116	
2-methyl pentane	0.341	0.272	1.106			0.385	0.244	
3-methyl pentane	0.394	0.186	1.276			0.276	0.151	
2, 2-dimethyl butane	0.033	0.050	0.120			0.098	0.070	
2, 3-dimethyl butane	0.082	0.074	0.265			0.075	0.116	
Methyl cyclohexane	0.065	0.118	0.202			0.104	0.041	
n-heptane	0.126	0.157	0.398		0.59	0.162	0.030	
2-methyl hexane	0.124	0.133	0.385			0.131		
3-methyl hexane	0.148	0.156	0.460			0.049	0.018	
2, 3-dimethyl pentane	0.080	0.115	0.252			0.050		
2, 4-dimethyl pentane	0.053	0.071	0.171			0.043		
2, 2, 3-trimethyl butane	0.009	0.012	0.031			0.048		
n-octane	0.062	0.085	0.197					
3-methyl heptane	0.042	0.082	0.131		0.08			
2-methyl heptane	0.054	0.102	0.171					
2, 2, 4-trimethyl pentane	0.148	0.576	0.476					
2, 3, 4-trimethyl pentane	0.055	0.170	0.171					
2, 3, 3-trimethyl pentane	0.061	0.209	0.194					
n-decane	4e-05		1e-4					
<i>Alkenes</i>								
Ethylene	1.343	1.372	4.564	4.92	5.33	1.659	2.107	7.534
Propylene	0.408	0.393	1.363	0.76	1.37	0.398	0.595	0.949
trans-2-pentene	0.032	0.057	0.097			0.090		
cis-2-pentene	0.016	0.029	0.050			0.112		
2-methyl-1-butene	0.076	0.102	0.250					
3-methyl-1-butene	0.018	0.037	0.058					
1-butene	0.041	0.058	0.139		0.21	0.229	0.071	
1-pentene	0.035	0.049	0.112					
cis-2-butene	0.017	0.030	0.059		0.10	0.097	0.107	
trans-2-butene	0.015	0.027	0.053		0.10		0.054	
Acetylene	1.000	1.000	3.6	4.99	3.94		1.000	1.271
<i>Aromatics</i>								
Styrene	0.007	0.012	0.026					0.023
Ethyl benzene	0.099	0.108	0.314		0.22	0.114	0.123	
(m + p)-xylene	0.387	0.346	1.159		0.64	0.351	0.330	
o-xylene	0.149	0.134	0.459	0.45	0.25	0.140	0.123	
1, 2, 4-trimethyl benzene	0.116	0.129	0.350			0.183	0.158	

Table 1. (continued)

Compound	Boston/New York City 2004, pptv [pptv C ₂ H ₂] ⁻¹	Boston/New York City 2002, pptv [pptv C ₂ H ₂] ⁻¹	Boston/New York City CO 2004, pptv [ppbv CO] ⁻¹	Los Angeles 2002, pptv [ppbv CO] ⁻¹	Boston/New York City (Baker et al., submitted manuscript, 2006), pptv [ppbv CO] ⁻¹	39 US Cities [Seila et al., 1989], pptv [pptv C ₂ H ₂] ⁻¹	Vehicle Exhaust [Harley et al., 1992], pptv [pptv C ₂ H ₂] ⁻¹	Database, pptv [ppbv CO] ⁻¹
1, 2, 3-trimethyl benzene	0.022	0.031	0.069			0.059	0.042	
1, 3, 5-trimethyl benzene	0.030	0.038	0.091			0.052	0.108	
1-ethyl-2-methyl benzene	0.033	0.036	0.100			0.050		
1-ethyl-(3 + 4)-methyl-benzene	0.116	0.124	0.349			0.140		
iso-propyl benzene	0.008	0.010	0.025					
n-propyl benzene	0.026	0.029	0.081					
Benzene	0.171	0.210	0.617	0.95	1.09	0.326	0.474	0.599
Toluene	0.846	0.792	2.622	3.51	3.79	0.749	0.967	6.439

^aThe estimated error on the measured emission ratios is 30%. Data in the first three columns were determined with the photochemical age method (see text) and therefore are the most accurate.

ratios by plotting VOC/CO versus the photochemical age would depend on the atmospheric background mixing ratio of CO and subtracting a constant CO background might lead to an error in the emission ratios. Plotting the ratio of acetylene with CO (with an atmospheric background of 75 ppbv subtracted [Warneke et al., 2006]) versus the photochemical age as described earlier yields an emission ratio of 3.9 pptv/ppbv. This value strongly depends on the estimated CO atmospheric background and on the different atmospheric life times (CO rate coefficient with OH is $2.4 \times 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ (1 atm and 298 K) [Atkinson et al., 2005]), which introduces a large uncertainty. We have therefore used the ratio between acetylene and CO of 3.6 pptv/ppbv as shown in Figure 2 to calculate the emission ratios versus CO. The data in Figure 2 are all the data measured on the RHB and WP-3 aircraft during the entire campaign; only biomass burning and power plants were eliminated. In Figure 2 the atmospheric background of CO of 75 ppbv that complicates the photochemical age method can also be seen. As will be shown in Figure 3, using the slope from the correlation plot of acetylene versus CO might cause a small error, which we estimate to be about 10% yielding a total error of the VOC/CO emission ratio of 40%.

[23] The standard method to determine emission ratios is to calculate the slope of the linear fit of the scatterplot of two compounds. Figure 3a shows the case of ethyl benzene versus acetylene. The color code indicates the photochemical age and it can be seen that the [ethyl benzene]/[acetylene] ratio is higher at younger ages. The linear fit through the data is given with the solid black line, which is usually used as the emission ratio. The emission ratio from the photochemical age method is shown with the red line in Figure 3a and lies close to all the points that have not been photochemically aged. The slope from the linear fit was determined for all the primary hydrocarbons listed in Table 1. The results are plotted in Figure 3b versus the photochemical age method from above. It can be seen that the values determined from the scatterplots are, for all compounds except two, lower than the method used here. Mixing with older air will cause the slopes from the correlation plots to change dependent on the lifetime and the mixing ratio of the investigated compounds in the aged air. The relative difference ($[\text{ER at photochem. Age } t = 0] - [\text{ER from } \Delta X]]/[\text{ER from } \Delta X]$) of the two methods is plotted versus the rate coefficient with OH in Figure 3c and it is obvious that there is a clear dependence on the lifetime of the investigated compound. The relative error gets larger the shorter-lived the compounds are. It is very difficult to get close enough to emission sources in ambient air measurements that neither mixing nor chemistry had changed the ratio of two compounds. We therefore will use the data determined with the photochemical age method for the further analysis in this paper. The [toluene]/[benzene] and [acetylene]/[CO] ERs, which cannot be determined with the photochemical age method, might therefore be an underestimation.

3.2. Emission Ratios of Oxygenated VOCs

[24] The calculation of the emission ratios of oxygenated VOCs (oxyVOCs) is further complicated by their photochemical production and possible biogenic sources

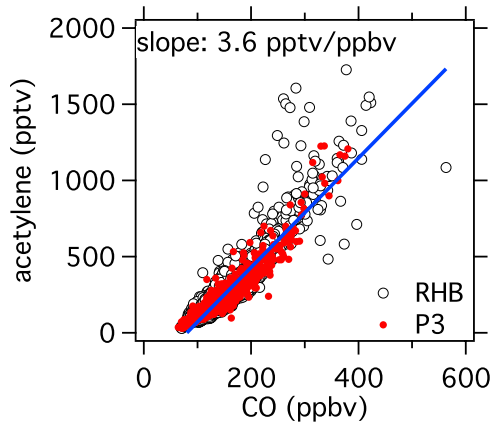


Figure 2. Scatterplot of acetylene versus CO for all the RHB ship (N = 1608) and all the WP-3 aircraft (N = 1065) measurements. The data were filtered for biomass burning and power plant plumes.

[de Gouw *et al.*, 2005; Li *et al.*, 1997]. Therefore no linear fit can be used in a semilogarithmic plot of the [oxyVOC]/[acetylene] ratio versus photochemical age. The evolution of oxyVOCs can be described using the expression [de Gouw *et al.*, 2005]:

$$\begin{aligned}
 [\text{oxyVOC}] = & ER_{\text{oxyVOC}} \times [\text{C}_2\text{H}_2] \\
 & \times \exp[-(k_{\text{oxyVOC}} - k_{\text{C}_2\text{H}_2})[\text{OH}]\Delta t] \\
 & + ER_{\text{precursor}} \times [\text{C}_2\text{H}_2] \times \frac{k_{\text{precursors}}}{k_{\text{oxyVOC}} - k_{\text{precursors}}} \\
 & \times \frac{\exp(-k_{\text{precursors}}[\text{OH}]\Delta t) - \exp(-k_{\text{oxyVOC}}[\text{OH}]\Delta t)}{\exp(k_{\text{C}_2\text{H}_2}[\text{OH}]\Delta t)} \\
 & + ([\text{biogenics}] + [\text{background}]) \quad (3)
 \end{aligned}$$

where the first term represents the removal of oxyVOCs by OH as described in equation (1). The second term represents the removal and production of secondary anthropogenic oxyVOCs. The third term represents biogenic emissions, including photochemical production from biogenics, plus the local background mixing ratios. ER_{oxyVOC} and $ER_{\text{precursor}}$ are the emission ratios of the oxyVOC and the precursor and $k_{\text{precursor}}$ the rate coefficient with OH from the precursor to form oxyVOCs. k_{oxyVOC} is the rate coefficient of the oxyVOC, which was taken from [Atkinson *et al.*, 2005]. Photolysis reactions of the oxygenated species are not taken into account, because the photolysis loss rate is small compared to the OH loss rate [Warneke *et al.*, 2004]. ER_{oxyVOC} , $ER_{\text{precursor}}$, $k_{\text{precursor}}$, $([\text{biogenics}] + [\text{background}])$ are determined from a linear least squares fit that minimizes the difference between the measured oxyVOC mixing ratio and those calculated from equation (3) [de Gouw *et al.*, 2005]. The results of this analysis for the emission ratios of the measured oxyVOCs on the RHB are shown in Table 2. All other parameters that can be determined from this fit are irrelevant to the analysis presented here and very similar to our previous study [de Gouw *et al.*, 2005] and are therefore not given. The non negligible influence of biomass burning from forest fires in Alaska and Canada [Warneke *et al.*, 2006] and the substantial ocean uptake of oxyVOCs further

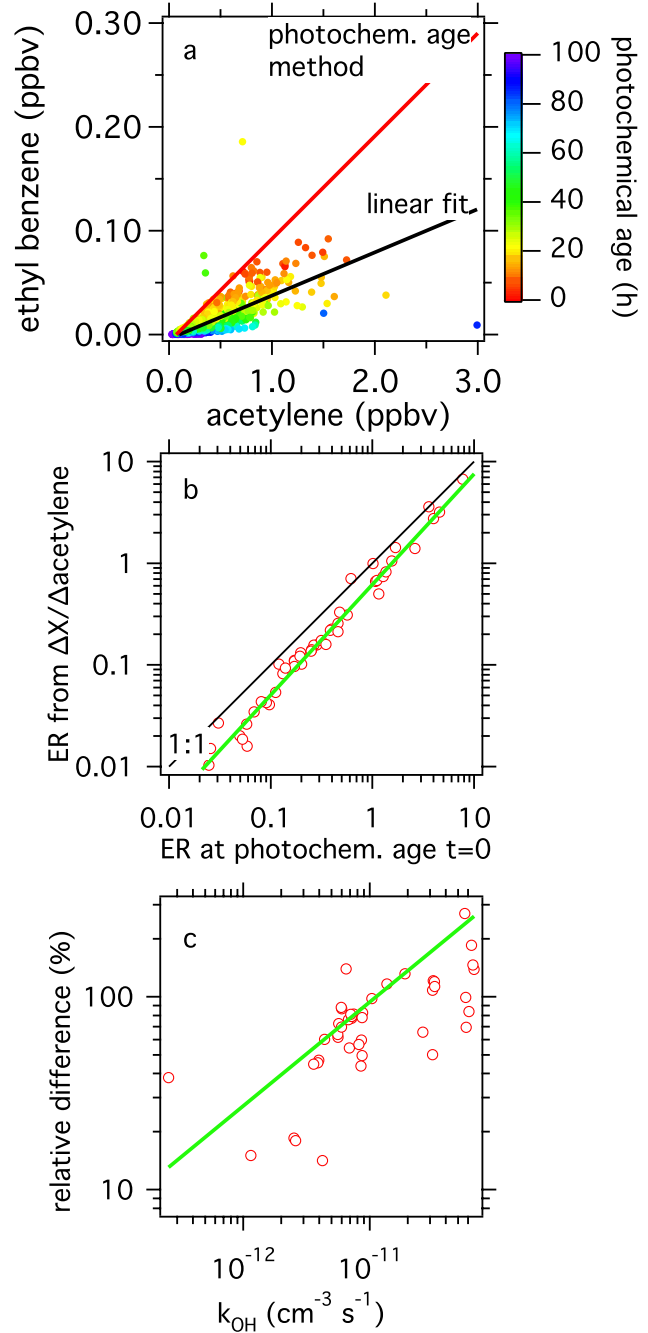


Figure 3. (a) Scatterplot of ethyl benzene versus acetylene (same data as Figure 1a). The black line is the linear fit, and the red line the emission ratio determined with the photochemical age method. (b) Emission ratios determined from scatterplots versus the ones determined with the photochemical age method for the 51 VOC species in Table 1, where each data point represents one compound. The emission ratios from the scatterplots are generally lower, because of mixing with aged air masses. (c) Relative difference of the two methods ($[\text{ER at photochem. Age } t = 0] - [\text{ER from } \Delta X]$)/ $[\text{ER from } \Delta X]$ versus the rate coefficient with OH. For shorter-lived compounds the difference is larger.

Table 2. Emission Ratios of Oxygenated VOCs

Compound	ER_{oxyVOC} (2004), pptv [pptv C ₂ H ₂] ⁻¹	ER_{oxyVOC} (2002), pptv [pptv C ₂ H ₂] ⁻¹	ER_{oxyVOC} (Slope Fresh Urban Plumes), pptv [ppbv CO] ⁻¹	ER_{oxyVOC} (2004), pptv [ppbv CO] ⁻¹	ER_{oxyVOC} (Los Angeles), pptv [ppbv CO] ⁻¹	ER_{oxyVOC} (Vehicle Exhaust), pptv [pptv C ₂ H ₂] ⁻¹	ER_{oxyVOC} (Database), pptv [ppbv CO] ⁻¹
Acetaldehyde	0.2	0.8	5.0	0.7	9.7	0.1	0.5
Propanal	0.2	0.2	n/a	0.7	n/a	0.01	
Acetone	0.8	1.2	5.8	2.9	14.2	0.1	0.5
MEK	0.2	0.3	2.0	0.8	1.5	0.01	
Methanol	1.1	2.3	9.0	4.0	8.4		0.1
Ethanol	1.6	1.0	n/a	5.8	n/a		
Acetic acid	0.0	0.0	3.2	0.0	n/a		

complicates the description of oxyVOCs versus the photochemical age and might result in an error in the determined emission ratios. We have therefore also calculated the emission ratios of the oxyVOCs measured with PTR-MS using the slopes of the linear fits of the scatterplots with CO from the fresh New York City and Boston plumes measured on board the WP-3 aircraft as explained previously. This is not possible for the hydrocarbons presented in Table 1 because of the limited number of canister samples taken in the plumes. The averaged emission ratios from all plume crossings are also given in Table 2. All of the emission ratios determined from the scatterplots are higher than from the photochemical age method, possibly indicating that substantial photochemical production had already increased the mixing ratios of the oxyVOCs even in the plumes thought to be “fresh.” The large difference shows that the emission ratios for oxyVOCs cannot be determined accurately from scatterplots.

[25] Here it should be mentioned that the emission ratios determined in this work are only valid for the total emissions of an urban area, which have a large contribution from on-road automobile emissions, but also include other urban sources such as emissions from off-road vehicles, point sources such as industrial facilities and area sources such as natural gas emissions and gasoline evaporation during transport and storage. The data presented here were collected downwind of the urban areas and therefore the different source categories cannot be distinguished, only the total “urban” emission ratios are determined.

[26] In the following section the results from Tables 1 and 2 are compared with other data sets and with the emission database used in air quality forecast models.

3.3. Comparison With Other Recent Data Sets

3.3.1. Comparison With Boston and New York City in 2002

[27] In 2002 the emission ratios relative to acetylene were determined on a cruise of the RHB in roughly the same area downwind of Boston and New York City [de Gouw *et al.*, 2005]. The comparison with the 2004 data is shown in Figure 4 and the values are given in Tables 1 and 2. The emission ratios for all four classes of compounds in both years generally agree within a factor of two as indicated by the shaded areas. Only the alkanes show some variability, which is not surprising, since a large part of the alkane emissions are area sources and are not completely dominated by automobile emissions, as will be discussed later. Also the oxyVOCs show some variability, which might be caused by

the ocean uptake or the larger uncertainties for those ERs. The agreement within a factor of two leads to three conclusions: (1) The emission ratios did not change significantly from 2002 to 2004, (2) the emissions were rather homogeneous in the whole New England region because in

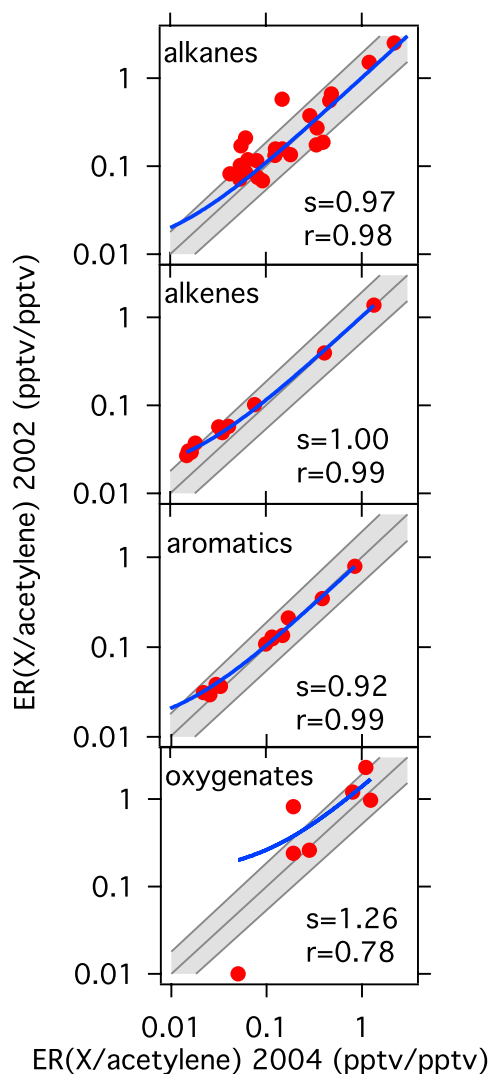


Figure 4. Comparison of the emission ratios from the 2002 and 2004 cruise with the RHB, where each data point represents one compound. The shaded area gives the agreement within a factor of 2. The blue lines are linear fits.

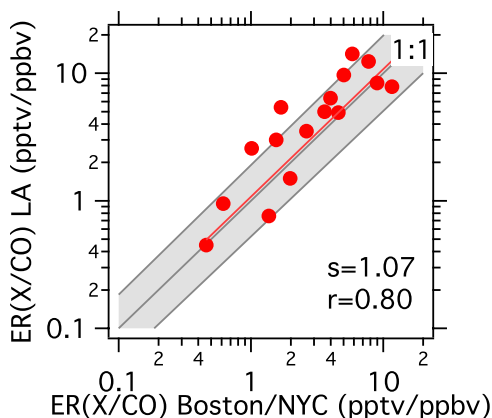


Figure 5. Comparison of the 2004 emission ratios with CO with data from a flight in the Los Angeles Basin in 2002, where each data point represents one compound. The solid red line is a linear fit through the data. The grey shaded area shows an agreement within a factor of two.

2004 the RHB spent significantly more time further north in the Gulf of Maine than in 2002, and (3) the method used here to determine the emission ratios yields results within a factor of two for different data sets.

3.3.2. Comparison With Los Angeles in 2002

[28] In the spring of 2002 the WP-3 conducted a research flight over the Los Angeles Basin [de Gouw *et al.*, 2003c; Neuman *et al.*, 2003]. During this flight the emission ratios for all available VOCs were determined using the slopes of the correlation plots with CO. The comparison with the results from Boston and New York City is shown in Figure 5 and the values are given in Tables 1 and 2. For a better comparison, the oxyVOCs plotted in Figure 5 from Boston and New York City were also determined from the slopes (column 3 in Table 2). The agreement is within a factor of two, except for the butanes, which might be strongly influenced by area sources and therefore dependent on the location, and for acetone and acetaldehyde. It is also interesting to note that during this flight the alkyl nitrates, which are photochemically produced, were rather low. This shows that photochemistry had only a small influence on the measured emissions ratios presented here. Even with slow photochemistry, some of the emission ratios from Los Angeles were higher than from Boston and New York City (both determined from the slopes). On the other hand, differences between cities are to be expected.

3.3.3. Comparison With Canister Samples From Boston and New York City

[29] A comparison with data taken from A. Baker *et al.* (Measurements of NMHCs in U.S. cities, submitted to *Journal of Geophysical Research*, 2006, hereinafter referred to as Baker *et al.*, submitted manuscript, 2006) is shown in Figure 6 and the values are given in Table 1. Baker *et al.* (submitted manuscript, 2006) collected whole air canister samples at different ground sites in 28 US cities including Boston and New York City. Samples were collected in Boston (22 canisters) and New York City (21 canisters) during August 2003 and analyzed using various GC techniques. Each canister was filled at a unique sampling site,

selected to be removed from point sources, and these sites were distributed throughout each city. The emission ratios were determined by the slope of the VOCs versus CO from all the canisters collected in both cities. The results of the two measurements correlate well ($R = 0.97$) with a slope of $S = 0.88$. The small difference in the slope might be caused by the difference in the methods used to determine the emissions ratios as was described previously in Figure 3b.

3.3.4. Comparison With Average Urban Air Composition and Vehicle Exhaust

[30] A comparison with the average urban air composition from 39 US cities published by Seila *et al.* is shown in Figure 7 [Seila *et al.*, 1989] and the data are given in Table 1. Even though this study is nearly two decades old, it is one of the most comprehensive measurements of urban air composition published, in contrast to tunnel studies that give detailed information about the vehicle exhaust. More recent studies of ambient urban air, such as by [Millet *et al.*, 2005] did not include acetylene or CO mixing ratios and cannot be used to compare to the data set presented here. It can be seen that our measured emission ratios also compare well with the Seila *et al.* data set. Mainly ethane and propane are higher in the New England data and *n*-butane is lower than the average composition. Also shown in Figure 7 and Tables 1 and 2 is a comparison with measurements from vehicle exhaust [Harley *et al.*, 1992]. The C_2 - C_4 alkane emission ratios measured here are higher than in the vehicle exhaust, because evaporation of gasoline and other area sources are an important source of these VOCs in an urban area [Harley *et al.*, 1992; Rubin *et al.*, 2006]. Most of the alkenes and aromatics are also within a factor of two with

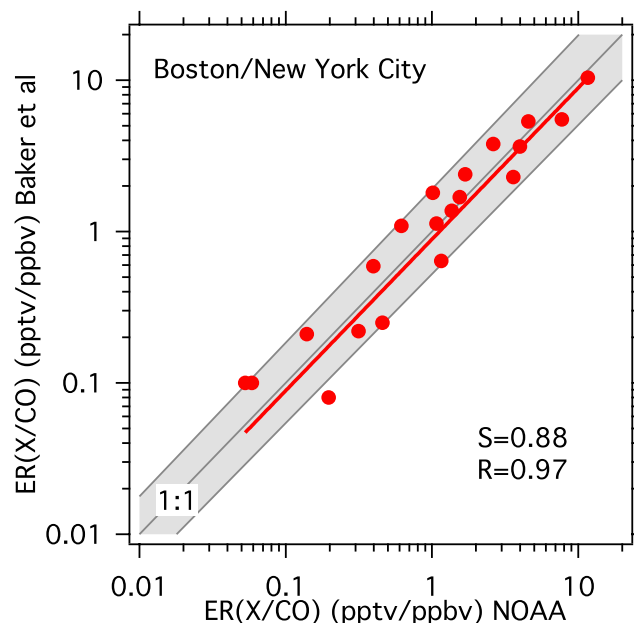


Figure 6. Comparison of the emission ratios with CO from 2004 with data from Baker *et al.* (submitted manuscript, 2006), which are canister samples collected in Boston and New York City. Each data point represents one compound, and the solid red line is a linear fit through the data. The grey shaded area shows an agreement within a factor of two.

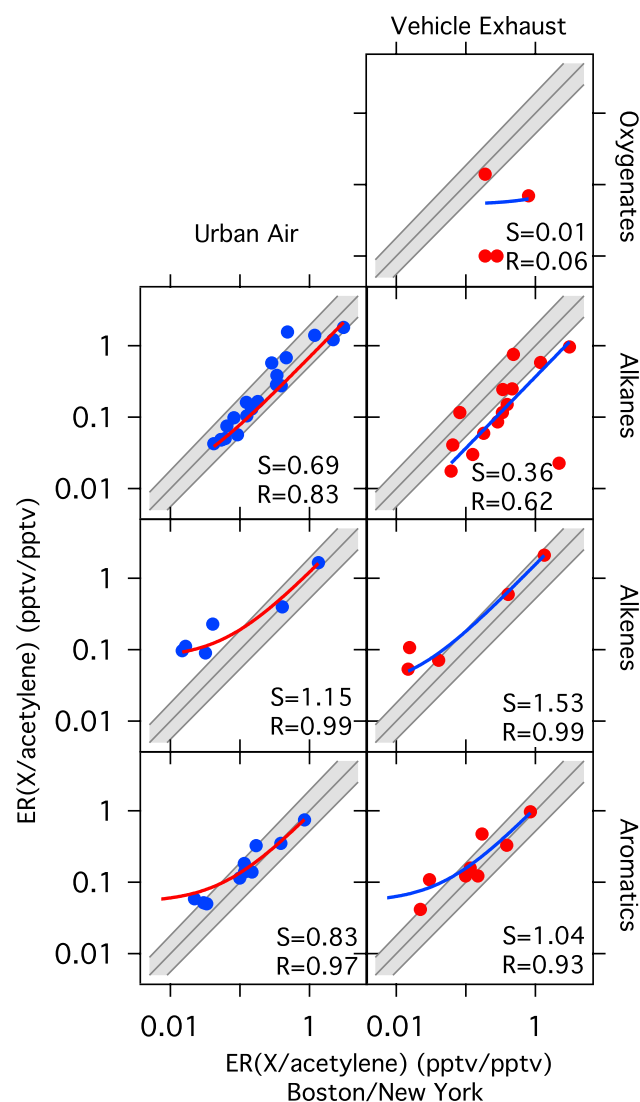


Figure 7. Comparison of the 2004 emission ratios with acetylene with average data of 39 U.S. cities [Seila *et al.*, 1989] and vehicle exhaust measurements [Harley *et al.*, 1992]. Each data point represents one compound, and the solid lines are linear fits through the data. The grey shaded area shows an agreement within a factor of two.

the vehicle exhaust measurements showing that mobile sources are a main source for those compounds in urban air. The oxyVOCs in the vehicle exhaust are smaller than in the urban measurements confirming that only small quantities are emitted by automobiles [de Gouw *et al.*, 2005].

[31] The emission ratios determined in this work generally agree well with recent measurements from urban areas even though these were done in different years or cities as shown in Figures 4–7. For alkenes and aromatics they also agree generally well with vehicle exhaust measurements. For individual compounds there are clear differences between the cities, years and seasons and in the Figures 4–7 the agreement of within a factor of 2 that we consider as a good agreement is shown with the grey shaded area. These differences can be caused for example by different fuel compositions, different industrial facilities, different evaporative sources, which are also dependent on ambient temperature, and many other possible differences between cities or years. Furthermore uncertainties in the measurements and the analysis can cause differences between the various data sets. A discussion about differences of individual species is beyond the scope of this paper and can be found elsewhere (Baker *et al.*, submitted manuscript, 2006).

[32] From the different data sets given in Table 1 the most accurate and up-to-date urban VOC emission ratios are determined by the photochemical age method, which are given in the first three columns. Those will be used in the further analysis.

3.4. Comparison With the Anthropogenic Emissions Database

[33] The anthropogenic VOC emissions database, based on the NEI-99 data, separates emissions into four categories: on-road, nonroad, point, and area sources. The on-road emissions are mobile sources, which are mainly highway gasoline and diesel cars and trucks, the nonroad are mobile sources, which are off-highway vehicles such as 2-stroke lawn and garden equipment or construction, farming and mining equipment, the area sources are evaporation during storage and transport of petroleum products like gasoline service stations or nonindustrial solvent evaporation, and the point sources are industrial operations or petroleum and solvent evaporation from, for example, surface coating operations. Small point sources are included in the area sources.

[34] To compare the measured emission ratios with the VOC emissions database we have integrated the gridded VOC emissions for all available species and CO in squares that cover Boston (latitude 42.1 to 42.5 and longitude –71.4 to –71.0, 1440 km²), New York City (latitude 40.5 to 41.3 and longitude –74.6 to –73.5, 8096 km²) and Los Angeles (latitude 33.5 to 34.3 and longitude –118.5 to –117.7, 5824 km²), respectively. The relative speciation of the four categories for the three cities, the total emissions and the emissions per square kilometer are given in Table 3. In Boston and New York City the area sources and in Los Angeles the on-road sources dominate. The point sources in

Table 3. Relative Contributions of the Different Source Categories to the VOC Emissions, the Total VOC Emissions, and the VOC Emissions per Square Kilometer of Boston, New York City, and Los Angeles

City	On-Road VOC Emission, %	Nonroad VOC Emission, %	Area VOC Emission, %	Point VOC Emission, %	Total VOC Emission, tons/day	VOC Emissions, kg/day/km ²
Boston	28	24	45	3	211	139
New York City	32	17	47	4	1210	149
Los Angeles	40	25	32	3	908	148

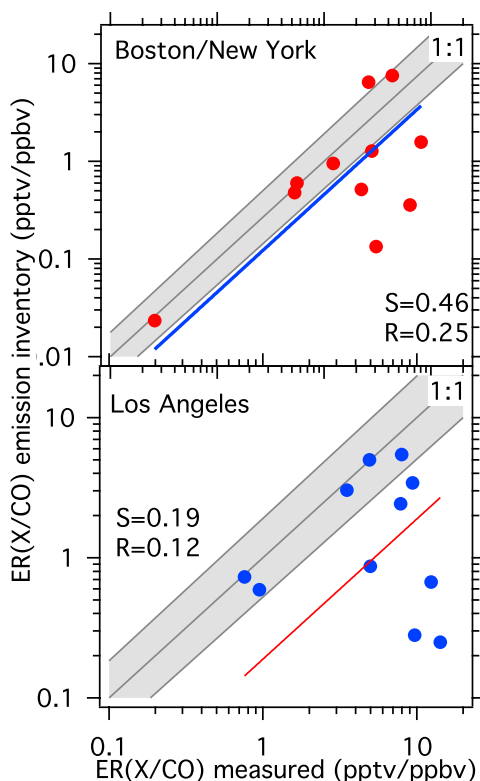


Figure 8. Comparison of the measured emission ratios with CO with an anthropogenic emissions database based on EPA NEI-99 data that is used in various air quality forecast models. Each data point represents one compound, and the solid lines are linear fits through the data. The grey shaded area shows an agreement within a factor of two.

all three cities are very small. In all three cities the emissions per square kilometer are about the same, but New York as the largest city has the largest total emissions.

[35] After summing up the four categories, the total VOC/CO ratios for individual and lumped species were calculated. The ratios for all the available individual species are given in Table 1 and the comparison for Boston/New York and Los Angeles with the measurements is shown in Figure 8. The measurements and the database do not agree well, especially the alkanes and oxygenated VOCs are very different.

[36] The main source for the alkanes are the area sources, which are the most difficult to determine accurately. In the emissions database the area sources are generally larger than the on-road emissions, but the good agreement of the measurements with the vehicle exhaust might indicate that the contribution of the area sources is overestimated in the database. Only recently it was shown that oxyVOCs are also emitted in large quantities from urban areas [e.g., *de Gouw et al.*, 2005; *Jacob et al.*, 2002, 2005; *Li et al.*, 1997; *Singh et al.*, 2001]. The sources of oxyVOCs in urban areas is not well understood yet, but they are likely not primary automobile emissions [*de Gouw et al.*, 2005]. The emissions database does not yet include those recent findings of large oxyVOC emissions, which cause the large discrepancies with the presented oxyVOC emission ratios.

[37] The measured emission ratios for different years and cities, as presented in Figures 4–7, certainly have a variability for individual species of up to a factor of two or more for certain species and different locations, but the differences are still small as compared to the difference with the emissions database from Figure 8.

[38] The emission input of a certain VOC into a chemical forecast model is crucial for the quality of the prediction of this species and as a result also for ozone and secondary organic aerosols. The prediction of toluene and CO from the WRF-CHEM model is compared in Figure 9 with the measurements of those two species. In Figure 9 an altitude profile of all the measurements from the WP-3 during the NEAQS-ITCT2004 campaign are compared with the WRF-CHEM results along the flight track. CO agrees fairly well, whereas toluene is overpredicted by almost a factor of 3, which is close to the difference in the emission ratios from the database and the measurements.

[39] The WRF-CHEM toluene results shown in Figure 9 are for the lumped RADM2 aromatic compound assigned to toluene. However, within the RADM2 reactivity weighted assignment to individual VOC emissions for this lumped species, more than 80% is due purely to toluene for the individual urban areas considered in this study, and for the entire U.S.

3.5. OH Reactivities

[40] The OH reactivity of a compound is calculated by multiplying its concentration with the OH rate coefficient (taken from *Atkinson et al.* [2005]). For this calculation the emission ratio and a CO enhancement of 100 ppbv was used, which is conservatively low for typical observed urban CO enhancements during NEAQS-ITCT2004. Shown in Figure 10 are the reactivities of CO (100 ppbv) and the different classes of compounds calculated from the measured emission ratios of the 2004 data. The total reactivity of all VOCs is about 50% larger than of CO. The alkanes, alkenes and aromatics contribute about equally to the VOC

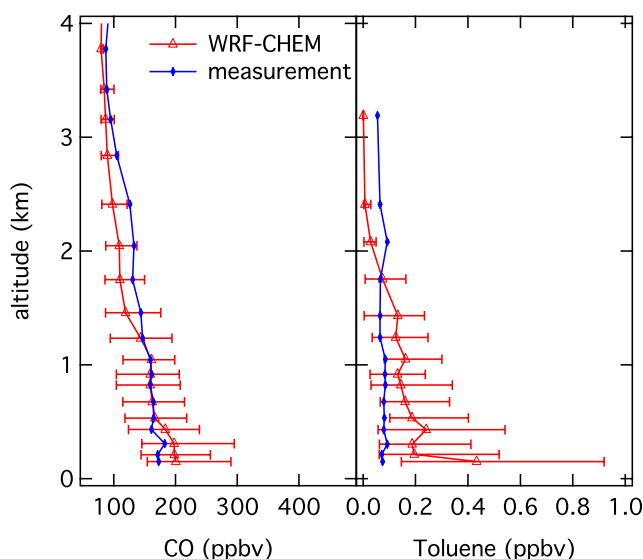


Figure 9. Measured and modeled altitude profiles of toluene and CO.

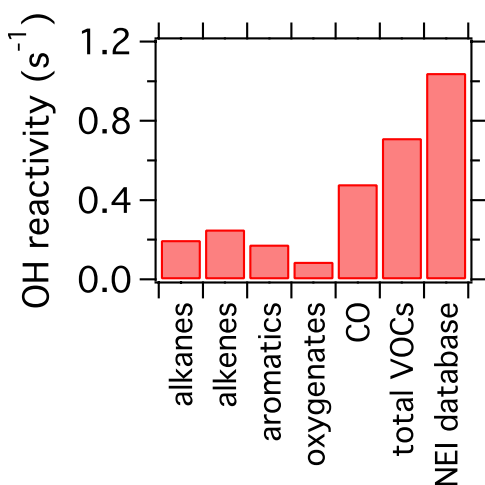


Figure 10. VOC and CO reactivities with OH calculated from the measured emission ratios and a CO enhancement of 100 ppbv. Different classes of compounds and all the VOCs included in the EPA NEI-99 based database are shown.

reactivity and the oxyVOCs only play a minor role at the time of the emission. The alkenes have the shortest lifetimes followed by the aromatics and the alkanes and therefore the reactivity in the early stages of the plume evolution will be dominated by the alkenes. Later as the plume ages and the short-lived alkenes and aromatics are reacted away the total reactivity will be smaller and dominated by the alkanes and oxyVOCs [Goldan *et al.*, 2004].

[41] Also shown in Figure 10 is the total reactivity of all the VOCs in the emissions database. The total reactivity of the database is about 30% larger than of the sum of the measured VOCs. The database includes more compounds in the lumped species than the measurements, but the ones that contribute most to the reactivity are measured. Using this database it might be difficult to predict individual compounds accurately as seen in Figure 9, but the rather small difference in total reactivity will help in the prediction of ozone.

4. Conclusion

[42] Emission ratios with CO of a large number of VOCs were determined for the urban areas Boston/New York City and Los Angeles and compared to other data sets. The measurements presented here compared well to other measurement data from urban areas and also to measurements of vehicle exhaust indicating that a large source of VOCs in urban areas is automobile exhaust. On the other hand the measured emission ratios did not compare well ($R = 0.29$, slope of 0.57) with a frequently used anthropogenic emissions database, especially the alkanes and the oxygenated VOCs showed discrepancies of up to an order of magnitude. The urban emissions in the database are dominated by area sources and not by the on-road emissions. The toluene mixing ratio calculated with the WRF-CHEM model in the New England using this database is overpredicted by about a factor of three. This is about the same difference as between database and measurements. Using measured emis-

sion ratios for urban areas instead of inventories could therefore in some cases help improve the quality of regional air quality forecast models. It is also important in future studies to find out the reasons for the discrepancies and apply the appropriate corrections to the speciation profiles of VOCs used in the inventories.

[43] **Acknowledgments.** We thank the crews of the NOAA WP-3 and Ronald H. Brown and our NEAQS-ITCT 2004 collaborators.

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